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 NEWS  3   Jan 25     Searching with the P indicator for Preparations
 NEWS  4   Jan 29     FSTA has been reloaded and moves to weekly updates
 NEWS  5   Feb 01     DKILIT now produced by FIZ Karlsruhe and has a new update
                      frequency
 NEWS  6   Feb 19     Access via Tymnet and SprintNet Eliminated Effective 3/31/02
 NEWS  7   Mar 08     Gene Names now available in BIOSIS
 NEWS  8   Mar 22     TOXLIT no longer available
 NEWS  9   Mar 22     TRCTHERMO no longer available
 NEWS 10   Mar 28     US Provisional Priorities searched with P in CA/CAplus
                      and USPATFULL

 NEWS EXPRESS    February 1 CURRENT WINDOWS VERSION IS V6.0d,
                 CURRENT MACINTOSH VERSION IS V6.0a(ENG) AND V6.0Ja(JP),
                 AND CURRENT DISCOVER FILE IS DATED 05 FEBRUARY 2002
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FILE COVERS 1907 - 21 Mar 2002 VOL 136 ISS 13
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The P indicator for Preparations was not generated for all of the
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Numbers with the P indicator executed between 12/27/01 and 1/23/02 may
be incomplete. See the NEWS message on this topic for more information.

```
=> s ligand (w) replacement
        209662 LIGAND
         89081 REPLACEMENT
L1         187 LIGAND (W) REPLACEMENT

=> s l1 and (chromium or cr)
        268966 CHROMIUM
        343444 CR
L2          14 L1 AND (CHROMIUM OR CR)

=> d l2 1-14 all
```

L2 ANSWER 1 OF 14 CA COPYRIGHT 2002 ACS
AN 129:141176 CA
TI Kinetic Study on the Substitution of Dimethylacetamide for the Terminal Aqua Ligands in the Trinuclear **Chromium**(III) Complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ (R = H, CH3, CH3CH2, CH2Cl, CHCl2, CH3OCH2, (CH3)3C, CH2ClCH2, (CH3CH2)2CH). Elucidation of the Mechanism from the Activation Volumes and the Substituent Effects of Bridging Carboxylate Ligands
AU Fujihara, Takashi; Aonahata, Jun; Kumakura, Shigekazu; Nagasawa, Akira; Murakami, Kazuhiro; Ito, Tasuku
CS Dep. Chem., Fac. Sci., Saitama Univ., Urawa, Saitama, 338-8570, Japan
SO Inorg. Chem. (1998), 37(15), 3779-3784
CODEN: INOCAJ; ISSN: 0020-1669
PB American Chemical Society
DT Journal
LA English
CC 67-3 (Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms)
Section cross-reference(s): 75, 78
AB The substitution of dimethylacetamide (dma) for the terminal aqua ligands in the carboxylate-bridged trinuclear **chromium**(III) complex [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ (R = H, CH3, CH3CH2, CH2Cl, CHCl2, CH3OCH2, (CH3)3C, CH2ClCH2, (CH3CH2)2CH) in dma was kinetically studied by UV-visible absorption at 25-50 .degree.C and 0.1-232 MPa. The time course is uniphasic over all three steps of the **ligand** **replacement**. The substitution rate k varied from 2.4(1) .times. 10-5 (R = CHCl2) to 9.49(2) .times. 10-3 (R = C(CH3)3) s-1 depending on the substituent R at 40 .degree.C. Large pos. activation parameters

.DELTA.H.thermod. (98-123 kJ mol-1), .DELTA.S.thermod. (29-81 J K-1 mol-1), and .DELTA.V.thermod. (12.4-21.3 cm3 mol-1) for all the complexes suggested a dissociative activation mode (D or Id mechanism). It is similar to those for terminal ligand substitution of acetate-bridged trinuclear complexes of ruthenium(III) and rhodium(III) with a .mu.3-O ligand and molybdenum with two .mu.3-O ligands. Examn. of the substituent effect disclosed a linear relationship between k and Taft's electronic parameters, as well as pKa (RCOOH), indicating that the .sigma.-donor ability of the bridging carboxylate affects the strength of the **Cr** -OH2 bond in the cis position. The crystals of [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3][B(C6H5)4].cntdot.nH2O (R = H (1b), n = 6; R = CH3 (2b), n = 2) were found to be triclinic with space group P.hivin.1, a = 9.2080(8) .ANG., b = 14.724(2) .ANG., and c = 15.308(2) .ANG., .alpha. = 79.369(6).degree., .beta. = 86.513(8).degree., .gamma. = 79.823(8).degree., Z = 2, and V = 2006.5(4) .ANG.3 and with space group P.hivin.1, a = 8.848(6) .ANG., b = 15.057(7) .ANG., c = 17.375(8) .ANG., .alpha. = 107.82(3).degree., .beta. = 104.57(4).degree., .gamma. = 92.27(4).degree., Z = 2, and V = 2116(2) .ANG.3, resp. The relatively longer **Cr**-OH2 distances (av. 2.03(1) and 2.06(2) .ANG. for 1b and 2b, resp.) than those of the mononuclear **chromium**(III) aqua complexes, due to a trans effect of the central oxide ion and the addnl. cis effect of the bridging carboxylate, play a role in accelerating the dissociative substitution for the terminal ligands.

ST kinetics deaquation trinuclear **chromium** complex; substitution kinetics trinuclear **chromium** complex; mechanism deaquation **chromium** complex activation vol; substituent effect bridging carboxylate **chromium** complex; crystal structure trinuclear **chromium** complex

IT Activation enthalpy
Activation entropy
Activation volume
Crystal structure
Deaquation
Deaquation kinetics
Molecular structure
Substituent effects
(kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols. and substituent effects of bridging carboxylate ligands)

IT Cluster compounds
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process)
(kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols. and substituent effects of bridging carboxylate ligands)

IT 210689-21-7P 210689-22-8P
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(crystal structure; kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols.)

IT 127-19-5, Dimethylacetamide
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process)
(kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols. and substituent effects of bridging carboxylate ligands)

IT 11078-96-9P 36502-05-3P 51187-06-5P 55351-89-8P 150226-61-2P 210689-16-0P 210689-17-1P 210689-18-2P 210689-19-3P
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process)

(kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols. and substituent effects of bridging carboxylate ligands)

IT 210689-23-9P 210689-25-1DP, carboxylate-bridged derivs.
RL: SPN (Synthetic preparation); PREP (Preparation)
(kinetics of substitution of dimethylacetamide for terminal aqua ligands in trinuclear **chromium**(III) complexes [Cr3(.mu.3-O)(.mu.-RCO2)6(H2O)3]+ and mechanism from activation vols. and substituent effects of bridging carboxylate ligands)

L2 ANSWER 2 OF 14 CA COPYRIGHT 2002 ACS

AN 128:96926 CA

TI Heterogeneous effects on the thermal and photoreactivities of tris(1,2-diaminoethane)**chromium**(III) cation and hexathiocyanatochromate(III) anion in aqueous media

AU Bharathi, Alagar; Muthumani, Narayanan; Anbalagan, Krishnamoorthy

CS Department of Chemistry, Gandhigram Rural Institute-Deemed University, Gandhigram, 624 302, India

SO Transition Met. Chem. (London) (1997), 22(6), 586-588
CODEN: TMCHDN; ISSN: 0340-4285

PB Chapman & Hall

DT Journal

LA English

CC 78-9 (Inorganic Chemicals and Reactions)
Section cross-reference(s): 67, 74

AB The ground- and excited-state reactivities of the [**Cr**(en)3]3+ (en = 1,2-diaminoethane) and [**Cr**(NCS)6]3- ions in a polyacrylamide (PAA) environment are reported. The aquation kinetics of these complexes was studied to identify the effect of added PAA with varying mol. wt. Aquation of the complexes in aq. acid contg. PAA yielded the resp. substituted products. The macromol. in soln. decreases significantly the rate of **ligand replacement**. Similarly, photolysis of the cationic and anionic complexes in water PAA mixts. revealed a decrease in aquation quantum yield. Possible explanations for the decrease in reaction rates and quantum yields are discussed.

ST **chromium** ethylenediamine thiocyanato aquation heterogeneous effect; ethylenediamine **chromium** aquation effect polyacrylamide addn; thiocyanato **chromium** aquation effect polyacrylamide addn; polyacrylamide addn effect aquation **chromium** complex; aquation kinetics trisethylenediaminechromium 3 polyacrylamide effect; photoaquation hexathiocyanatochromate polyacrylamide effect

IT Photosubstitution reaction
(coordinative; aquation of tris(diaminoethane)**chromium**(3+) and hexathiocyanatochromate(3-) as a function of mol. wt. of added polyacrylamide)

IT Aquation kinetics
(of tris(diaminoethane)**chromium**(3+) and hexathiocyanatochromate(3-) as a function of mol. wt. of added polyacrylamide)

IT Coordinative substitution reaction
(photochem.; aquation of tris(diaminoethane)**chromium**(3+) and hexathiocyanatochromate(3-) as a function of mol. wt. of added polyacrylamide)

IT Aquation
(photochem.; of tris(diaminoethane)**chromium**(3+) and hexathiocyanatochromate(3-) as a function of mol. wt. of added polyacrylamide)

IT 14282-33-8 71723-95-0
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process)
(aquation kinetics and photoaquation as a function of added polyacrylamide)

IT 9003-05-8, Polyacrylamide
RL: NUU (Other use, unclassified); USES (Uses)
(effect on aquation of tris(diaminoethane)**chromium**(3+) and hexathiocyanatochromate(3-))
IT 25884-85-9, Diaquabis(ethylenediamine)**chromium**(3+) 30178-32-6
RL: FMU (Formation, unclassified); FORM (Formation, nonpreparative)
(formation from thermal and photoaquations of tris(1,2-diaminoethane) **chromium**(3+))

L2 ANSWER 3 OF 14 CA
AN 124:289820 CA
TI Synthesis of Bis(.eta.2-alkyne) Trinuclear Zwitterionic Platinum Hydride Complexes by Reaction of [trans-Pt(C6F5)2(C.tplbond.**CR**)2]2- with the Solvento Species [trans-PtHL2(acetone)]+
AU Ara, Irene; Berenguer, Jesus R.; Fornies, Juan; Lalinde, Elena; Moreno, M. Teresa
CS Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-Consejo Superior de Investigaciones Cientificas, Zaragoza, 50009, Spain
SO Organometallics (1996), 15(7), 1820-5
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
CC 29-13 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 75
AB The alkynylation of trans-[Pt(C6F5)2(tht)2] (tht = tetrahydrothiophene) with LiC.tplbond.**CR** in di-Et ether (R = Ph, SiMe3) or THF (R = tBu) leads to novel dianionic species [trans-Pt(C6F5)2(C.tplbond. **CR**)2]2- (R = Ph (1), SiMe3 (2), tBu (3)) which have been isolated as tetrabutylammonium salts. Treatment of (NBu4)2[trans-Pt(C6F5)2(C.tplbond.**CR**)2] (R = Ph, SiMe3, tBu) with 2 equiv of cationic hydride reagents of the type [trans-PtHL2(acetone)]+ (L = PPh3, PEt3) in acetone form, via a **ligand replacement**, simple bis(.eta.2-alkyne) trinuclear zwitterionic complexes trans,trans,trans-{[Pt(C6F5)2(.mu.-.eta.1:.eta.2-C.tplbond.**CR**)2](PtHL2)2} (R = Ph, L = PPh3 (4a), PEt3 (4b); R = SiMe3, L = PPh3 (5a), PEt3 (5b); R = tBu, L = PEt3 (6b)). The structure of complex 4b has been detd. by x-ray diffraction methods.
ST alkyne trinuclear zwitterionic platinum hydride prepn; crystal structure bisalkyne platinum trinuclear complex; mol structure bisalkyne platinum trinuclear complex
IT Alkynylation
(of bis(pentafluorophenyl)bis(tetrahydrothiophene)platinum complex)
IT Crystal structure
Molecular structure
(of bisalkyne platinum trinuclear complex)
IT 74464-76-9
RL: RCT (Reactant)
(alkynylation of)
IT 536-74-3, Phenylacetylene 917-92-0, tert-Butylacetylene 1066-54-2, Trimethylsilylacetylene
RL: RCT (Reactant)
(alkynylation of bis(pentafluorophenyl)bis(tetrahydrothiophene)platinum complex with)
IT 175474-46-1P
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and crystal structure of)
IT 175671-18-8P 175671-20-2P 175671-22-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and reaction with platinum hydride solvento complex)
IT 175474-43-8P 175474-44-9P 175474-45-0P 175474-47-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
IT 16841-99-9, trans-Chlorohydrobis(triphenylphosphine)platinum 16842-17-4,

trans-Hydridochlorbis(triethylphosphine)platinum 175474-48-3
175474-49-4
RL: RCT (Reactant)
(reaction with bis(alkyne)platinum complex)

L2 ANSWER 4 OF 14 CA
AN 120:218052 CA
TI Transformation of the C2H ligand in Fp*C.tplbond.CH [Fp* = (.eta.5-C5Me5)Fe(CO)2] into various C2 functional groups via an iron-substituted vinylidene complex, (.eta.5-C5H4Me)Mn(CO)2[:C:C(H)Fp*]: its amphoteric reactivities, structural comparisons relevant to 1-alkyne-to-vinylidene rearrangements, and electronic influences on structures of heterobimetallic bridging alkynyl complexes [(.eta.5-C5R5)M(CO)2]2(.mu.-C2R)
AU Akita, Munetaka; Ishii, Naomi; Takabuchi, Akio; Tanaka, Masako; Moro-oka, Yoshihiko
CS Res. Lab. Resourc. Util., Tokyo Inst. Technol., Yokohama, 227, Japan
SO Organometallics (1994), 13(1), 258-68
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
CC 29-12 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 75
OS CASREACT 120:218052
AB The iron-substituted vinylidene complex Cp'Mn(CO)2[:C:C(H)Fp*] (4) forms via a **ligand replacement** of Cp'Mn(CO)2(THF) with Fp*C.tplbond.CH (3) followed by a 1,2-H shift. 4 Has been characterized as a hybrid of the .eta.1-vinylidene structure (4B, the dominant contributor) and the zwitterionic structure [Cp'Mn-(CO)2C.tplbond.CH]Fp*+ (4D) in contrast to previously reported dinuclear bridging alkynyl complexes M1M2(.mu.-C2R) which lie between the .eta.2-alkyne complex type structure (.eta.2-M1C.tplbond.**CR**)M2 (A) and the .eta.1-vinylidene structure M1:C:C(R)M2 (B). The C2H ligand in 4 is transformed successfully to various elementary C2 species via simple acid-base reactions. Deprotonation of 4 with n-BuLi generates an anionic ethynediyl intermediate, Li[Cp'Mn(CO)2C2Fp*] (6), and both of its bridging carbon atoms, on treatment with electrophiles, serve as a reaction site depending on their size. The reaction with H+ (a small electrophile) is an orbital-controlled one to regenerate 4 through protonation at the slightly more neg. charged C.beta. (adjacent to Fe) with the larger HOMO coeff., whereas the reaction at C.beta. with MeI (a bulky electrophile) is hindered by the sterically congested Cp* ligand to produce the .eta.2-alkyne complex Cp'Mn(CO)2(.eta.2-Fp*C.tplbond.CMe) (7) through methylation at C.alpha. (adjacent to Mn). On the other hand, 4 is readily protonated at C.beta. to give the cationic .mu.-vinylidene complex [Cp'Mn(CO)2Fp*(.mu.-C:CH2)]BF4 (8-BF4) via an Fe slippage. Redn. of 8+ with NEt4BH4 affords the vinyl complex Fp*CH:CH2 (9) by way of hydride addn. to the bridging carbon atom in 8+. EHMO calcns. on M1M2(.mu.-C2R) (a hybrid of A, B, and D) including 4 and 7 reveal that its structure depends on a balance of .pi.-electron-donating abilities of M1 and M2. As one of the two metal centers becomes more electron donating and the other becomes less so, the structure changes from A and B. Related mono- and dinuclear complexes can be arranged according to the structural continuum A-B which is consistent with the electron-donating abilities of the metal centers. In addn., the MO characteristics obsd. for the structural change A .fwdarw. B are very similar to those of the intramol. 1,2-H shift mechanism proposed for the 1-alkyne-to-vinylidene ligand rearrangement within a metal coordination sphere and thus the dinuclear complexes can be viewed as intermediate states of the 1,2-H shift.
ST iron substituted manganese vinylidene complex; alkyne vinylidene ligand rearrangement; crystal structure iron manganese bridged complex; mol structure iron manganese bridged complex
IT Rearrangement
(alkyne-to-vinylidene rearrangement within a metal coordination sphere)

IT Hydrogen shift
(in alkyne-to-vinylidene ligand rearrangement within a metal coordination sphere)
IT Crystal structure
Molecular structure
(of iron manganese bridged complexes)
IT 153957-26-7 153957-27-8
RL: RCT (Reactant)
(EHMO calcns.)
IT 153956-84-4 153956-85-5
RL: RCT (Reactant)
(crystal structure)
IT 1333-74-0
RL: RCT (Reactant)
(hydrogen shift, in alkyne-to-vinylidene ligand rearrangement within a metal coordination sphere)
IT 153956-87-7P
RL: SPN (Synthetic preparation); PREP (Preparation)
(intermediate in prepn. of iron manganese bridged complexes)
IT 153956-86-6P 153956-89-9P 153956-90-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
IT 1826-67-1, Vinylmagnesium bromide 88363-26-2
RL: RCT (Reactant)
(reactant, in prepn. of iron complex)
IT 12108-13-3 125453-83-0
RL: RCT (Reactant)
(reactant, in prepn. of iron manganese bridged complexes)

L2 ANSWER 5 OF 14 CA
AN 120:22145 CA
TI Diamagnetic behavior of high-resolution nitrogen-14 nuclear magnetic resonance spectra for coordinated nitrogens in paramagnetic **chromium**(III) diamine complexes
AU Fujihara, Takashi; Kaizaki, Sumio
CS Fac. Sci., Osaka Univ., Toyonaka, 560, Japan
SO J. Chem. Soc., Dalton Trans. (1993), (16), 2521-4
CODEN: JCDTBI; ISSN: 0300-9246
DT Journal
LA English
CC 77-7 (Magnetic Phenomena)
AB Diamagnetic behavior in the chem. shift and linewidth of high-resoln. nitrogen-14 NMR spectra for paramagnetic **chromium**(III) diamine complexes was studied in comparison with that for the corresponding diamine dihydrochlorides and the diamagnetic cobalt(III) complexes. The NMR signals can be assigned to each inequiv. nitrogen ligating atom of unsym. diamines in the **chromium**(III) complexes. The 14N NMR spectra are affected by the diamine chelate ring conformations of the tris(diamine) complexes, but hardly sensitive to the **ligand replacement** in trans- and cis-[CrX2(diamine)2] type complexes.
ST nitrogen NMR **chromium** cobalt diamine complex
IT Amines, properties
RL: PRP (Properties)
(**chromium**, nitrogen-14 NMR of)
IT Amines, properties
RL: PRP (Properties)
(cobalt, nitrogen-14 NMR of)
IT Nuclear magnetic resonance
(of **chromium** and cobalt diamine complexes, nitrogen-14)
IT 15053-78-8
RL: PRP (Properties)
(NMR spectra of diastereoisomers of, nitrogen-14)
IT 7440-47-3D, **Chromium**, diamine complexes 7440-48-4D, Cobalt, diamine complexes 10534-89-1 13408-73-6 13820-25-2 14023-00-8

14240-27-8   14240-29-0   14301-97-4   14516-62-2   15040-49-0
15040-50-3   15242-48-5   15444-78-7   16702-61-7   16827-48-8
17978-78-8   18042-08-5   19581-04-5   19581-07-8   27712-11-4
30321-01-8   36965-94-3   37381-44-5   58602-38-3   67327-02-0
96427-16-6   151736-53-7   151736-55-9   151736-57-1   151757-11-8
RL: PRP (Properties)
(NMR spectra of, nitrogen-14)

L2 ANSWER 6 OF 14 CA COPYRIGHT 2002 ACS
AN 103:31510 CA
TI Amorphous aluminosilicates containing trivalent **chromium** in a non-octahedral coordination environment
AU Stojakovic, Djordje; Vasovic, Dusanka
CS Fac. Technol. Metall., Univ. Belgrade, Belgrade, YU-11000, Yugoslavia
SO Monatsh. Chem. (1985), 116(5), 581-9
CODEN: MOCMB7; ISSN: 0026-9247
DT Journal
LA English
CC 78-6 (Inorganic Chemicals and Reactions)
AB Amorphous aluminosilicates contg. .ltoreq.5.8 wt.% **Cr** were prepd. by cation exchange on an amorphous Na aluminosilicate by using **Cr**(III) salts. Electronic spectroscopy has shown that the ligand arrangement around the **Cr**(III) sites does not correspond to the octahedral geometry. No isomorphous substitution of Al3+ by Cr3+ in the aluminosilicate occurs, and retroexchange of **Cr** by Na+ ions is not possible. The amorphous **Cr**-substituted aluminosilicates (ACSAS) are slightly acidic and when heated in air at 800.degree. no oxidn. of **Cr**(III) takes place. The **Cr** species in the ACSAS undergoes **ligand replacement** reactions with ethylenediamine.
ST aluminosilicate **chromium** amorphous; silicate alumino **chromium** amorphous ethylenediamine
IT Energy level splitting
(crystal-field, of **chromium** ethylenediamine complex in aluminum **chromium** silicate)
IT 13820-85-4   27535-70-2
RL: RCT (Reactant)
(cation exchange by, with amorphous sodium aluminosilicate)
IT 107-15-3DP, **chromium** complex in aluminum **chromium** silicate   7440-47-3DP, complex with ethylenediamine in aluminum **chromium** silicate
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. and Racah parameter of)
IT 57485-28-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn., Racah parameter, thermal stability and reaction with ethylenediamine)
IT 1344-00-9
RL: RCT (Reactant)
(sodium exchange in, by chromic ion)

L2 ANSWER 7 OF 14 CA COPYRIGHT 2002 ACS
AN 98:190576 CA
TI Synthesis, characterization, and properties of stable **chromium** (III) aryl isocyanide complexes
AU Bohling, David A.; Mann, Kent R.
CS Dep. Chem., Univ. Minnesota, Minneapolis, MN, 55455, USA
SO Inorg. Chem. (1983), 22(10), 1561-3
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
CC 78-7 (Inorganic Chemicals and Reactions)
Section cross-reference(s): 29
AB Several of the previously unavailable hexakis(aryl isocyanide) complexes

of **Cr**(III), **Cr**(CNAr)63+, were prepd. via the oxidn. of [**Cr**(CNAr)6]0 with the powerful oxidants NO+ and SbCl5. **Cr**(CNAr)6(SbCl6)3 (CNAr = Ph isocyanide, 2,6-dimethylphenyl isocyanide and 2,6-diisopropylphenyl isocyanide) and **Cr** (CNAr)6(BF4)3 (CNAr = 2,6-dimethylphenyl isocyanide) were obtained as stable, highly-colored microcrystals. These compds. are extremely powerful oxidants which undergo redn. upon exposure to the atm. The isocyanide ligands in these **Cr**(III) complexes exhibit extreme lability in typical org. solvents, the **ligand replacement** reactions occurring on dissoln. at room temp.

ST **chromium** 3 aryl isocyanide complex; oxidn **chromium** aryl isocyanide; phenyl isocyanide **chromium** complex; methylphenyl isocyanide **chromium** complex; isopropyl isocyanide **chromium** complex; redn **chromium** 3 dimethylphenyl isocyanide

IT Oxidizing agents
(**chromium**(III) aryl isocyanide complexes)

IT Substitution reaction
(of **chromium** aryl isocyanide complexes)

IT Oxidation
(of **chromium** aryl isocyanide complexes by nitrosyl salts or antimony pentachloride)

IT Reduction
(of **chromium**(III) dimethylphenyl isocyanide complex in air)

IT Magnetic moment
(of hexakis(dimethylphenyl isocyanide)**chromium**(3+) tris(tetrafluoroborate))

IT 82456-65-3 82456-71-1
RL: RCT (Reactant)
(oxidn. of, by antimony pentachloride)

IT 85135-18-8
RL: RCT (Reactant)
(oxidn. of, by nitrosyl tetrafluoroborate)

IT 17375-15-4
RL: RCT (Reactant)
(oxidn. of, by nitrosyl tetrafluoroborate or hexafluorophosphate or antimony pentachloride)

IT 85135-15-5P 85135-16-6P 85135-17-7P 85150-70-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

IT 85135-14-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn., magnetic moment and redn. of)

L2 ANSWER 8 OF 14 CA COPYRIGHT 2002 ACS

AN 97:173700 CA

TI EPR study of ligand-substitution reactions in nitrosyl complexes of **chromium**

AU Chuikova, A. I.; Ivantsov, A. E.; Ovchinnikov, I. V.; Akhmetov, N. S.; Kondrat'eva, O. I.

CS USSR

SO Deposited Doc. (1981), SPSTL 312 khp-D81, 21 pp. Avail.: SPSTL

DT Report

LA Russian

CC 77-6 (Magnetic Phenomena)
Section cross-reference(s): 78

AB Complex formation of pentaaquanitrosyl **Cr** with S-contg. ligands was studied by EPR. The compn. and structure of the formed complex were established. Processes of **ligand replacement** were examd. As chelate S-contg. ligands, K ethylxanthogenate, Na diethyldithiocarbamate, and diethyldithiophosphoric acid were used.

ST EPR **chromium** nitrosyl ligand substitution; ethylxanthogenate **chromium** nitrosyl EPOr; ethylthiocarbamate **chromium** nitrosyl EPR; thiophosphate **chromium** nitrosyl EPR; xanthogenate

chromium nitrosyl EPR
IT Electron spin resonance
(of **chromium** nitrosyl complex ligand-substition reaction)
IT 147-84-2D, nitrosyl **chromium** complexes 151-01-9D, nitrosyl **chromium** complexes 298-06-6D, nitrosyl **chromium** complexes
RL: PRP (Properties)
(ESR study of formation of)
IT 7440-47-3D, nitrosyl complexes
RL: PRP (Properties)
(ESR study of ligand-substituted reactions in)
IT 14951-34-9
RL: PRP (Properties)
(ESR study of ligand-substitution reactions in)
IT 140-89-6 148-18-5 298-06-6
RL: RCT (Reactant)
(reaction of, with nitrosyl complexes of **chromium**, ESR study of)

L2 ANSWER 9 OF 14 CA COPYRIGHT 2002 ACS
AN 93:167146 CA
TI Kinetics studies of ligand dissociation from bis-substituted derivatives of hexacarbonylchromium, trans-**Cr**(CO)4L2 (L = P(C4H9)3, P(OC6H5)3, P(OCH3)3, P(C6H5)3, and As(C6H5)3)
AU Wovkulich, Michael J.; Feinberg, Samuel J.; Atwood, Jim D.
CS Dep. Chem., State Univ. New York, Buffalo, NY, 14214, USA
SO Inorg. Chem. (1980), 19(9), 2608-11
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
CC 22-3 (Physical Organic Chemistry)
AB The kinetics of **ligand replacement** on trans-**Cr**(CO)4L2 (L = P(OPh)3, PBu3, and P(OMe)3 by CO was studied between 100 to 140.degree. in decane. The reactions proceed by rate-detg. dissocn. of the ligand L. Qual. data are also reported for **Cr**(CO)4(PPh3)2 and **Cr**(CO)4(AsPh3)2. The ordering of dissocn. rates, AsPh3 > PPh3 > PBu3 > P(OPh)3 > CO > P(OMe)3, is consistent with a very strong dependence of the .pi.-bonding capability of the ligand, in contrast to dissocns. from **Cr**(CO)5L. Activation parameters are presented for dissocns. of P(OPh)3, PBu3, and P(OMe)3.
ST kinetics ligand dissocn; exchange ligand kinetics; **chromium** phosphine phosphite
IT Carbonyls
RL: PRP (Properties)
(**chromium**, kinetics of ligand dissocn. of phosphine complexes)
IT Kinetics of exchange reaction
(ligand, of **chromium** phosphine and phosphite complexes)
IT 13007-92-6
RL: PRP (Properties)
(complexation with phosphines)
IT 14917-12-5 18461-34-2 18461-39-7 18497-59-1 20957-93-1 21370-42-3 29742-98-1 35039-06-6 38800-75-8 74034-37-0
RL: PROC (Process)
(kinetics of ligand dissocn. of)

L2 ANSWER 10 OF 14 CA COPYRIGHT 2002 ACS
AN 89:107397 CA
TI Arene-**chromium** complexes: photochemical substitution of phosphine and phosphite ligands by olefin
AU Donnini, G. Paul; Shaver, Alan
CS Dep. Chem., McGill Univ., Montreal, Que., Can.
SO Can. J. Chem. (1978), 56(11), 1477-81
CODEN: CJCHAG; ISSN: 0008-4042

DT Journal
LA English
CC 22-4 (Physical Organic Chemistry)
AB Complexes of the type (.eta.6-C6H5XCH2CH:CH2)**Cr**(CO)2L [X = O, CH2; L = PPh3, P(OPh)3, P(OEt)3, PMe2Ph], on UV irradn., undergo rapid displacement of L and coordination of the pendant olefin. (1,3,5-Me3C6H3) **Cr**(CO)2PPh3 undergoes the same reaction in the presence of cis-cyclooctene. These observations are related to the general inability to substitute a 2nd carbonyl ligand in (arene)**Cr**(CO)2Y by photochem. methods. Two compds. (.eta.6-C6H5XCH2CH:CH2)**Cr** (CO)2CS decomp. under UV irradn.
ST carbonyl **chromium** phosphine photolysis; allyloxybenzene **chromium** photochem ring closure
IT Carbonyls
RL: PRP (Properties)
(arenechromium phosphine complexes, photolysis of)
IT Photolysis
(of arenechromium carbonyl phosphine complexes)
IT Ring closure and formation
(photochem., arenechromium complexes)
IT 931-87-3
RL: PRP (Properties)
(irradn. of arenechromium carbonyl phosphine complex in presence of)
IT 12129-67-8
RL: PROC (Process)
(irradn. of, in presence of cyclooctene)
IT 57003-09-5 57003-12-0
RL: PRP (Properties)
(**ligand replacement** in)
IT 67454-63-1 67454-64-2 67454-65-3 67454-66-4 67454-67-5
RL: RCT (Reactant)
(photolysis of)
IT 12278-95-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. and irradn. of, in presence of cyclooctene)
IT 67481-67-8P 67481-68-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
(prepn. and photolysis of)
IT 67454-86-8P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
IT 57003-14-2 57003-17-5
RL: RCT (Reactant)
(reaction of, with phosphines)

L2 ANSWER 11 OF 14 CA COPYRIGHT 2002 ACS
AN 83:137457 CA
TI Kinetics of dissociation of the **chromium**(II) acetate dimer
AU Cannon, Roderick D.; Stillman, Jennifer S.
CS Sch. Chem. Sci., Univ. East Anglia, Norwich, Engl.
SO Inorg. Chem. (1975), 14(9), 2207-14
CODEN: INOCAJ
DT Journal
LA English
CC 67-3 (Catalysis and Reaction Kinetics)
AB The complex tetra-.mu.-acetato-dichromium(II) reacts in acetate buffer media with EDTA and other polydentate ligands to form monomeric **Cr** (II) complexes and with various oxidants to form **Cr**(III). **Ligand replacement** reactions and oxidns. by Co(NH3)5Cl2+ and Co(C2O4)33- conform to the rate law -d[Cr2[Cr2(OAc)4]/dt kD[Cr2(OAc)4] all with the same rate const. and activation parameters. Other slower oxidns. conform to the rate law -2d[Cr2(OAc)4]/dt = kA[Cr2(OAc)4]0.5[oxidant] where dA = kMKD0.5; KD is interpreted as the dissocn. const. of the equil. Cr2(OAc)4 .dblarw. 2Cr(OAc)2 and kM varies

with the nature of the oxidant. At 25.degree. and ionic strength 1.0 M (NaClO4), kD = 505 .+-. 50 sec-1, .DELTA.HD* = 14.3 kcal mole-1 and .DELTA.SD* .simeq. 3 cal degree-1 mole-1; for Co(III) complex, kA = 2.9 .times. 102 M-0.5 Su-1, .DELTA.HA* = 9.6 kcal mole-1, and .DELTA.SA* = -15 cal degree-1 mole-1; for Co(NH3)5OH2+ at 5.degree., kA = 1.7 .times. 104 M-0.5 sec-1. The rate const. kD is ascribed to an unimol. dissocn. of the binuclear CrII complex and its magnitude is rationalized in terms of a simple crystal field model.

ST **chromium** acetate dissocn kinetics; acetatochromium dissocn kinetics; substitution acetatochromium cobalt complex; oxidn acetatochromium cobalt complex

IT Ammines
RL: USES (Uses)
(cobalt, dichromium acetato complex reactions with)

IT Kinetics of dissociation
(of tetraacetatodichromium)

IT Kinetics, reaction
(of tetraacetatodichromium, with cobalt complexes)

IT 15020-15-2
RL: RCT (Reactant)
(dissocn. and cobalt complex reactions of, kinetics of)

IT 13291-61-7 14403-82-8 14970-14-0 15053-34-6 15136-66-0
RL: RCT (Reactant)
(reaction of, with tetraacetatodichromium, kinetics of)

IT 60-00-4, reactions
RL: RCT (Reactant)
(with tetraacetatodichromium, kinetics of)

L2 ANSWER 12 OF 14 CA

AN 81:54777 CA

TI Kinetics and mechanism of the reduction of tetrakis(4-N-methylpyridyl)porphinecobalt(III) by **chromium**(II)

AU Pasternack, Robert F.; Sutin, Norman

CS Dep. Chem., Ithaca Coll., Ithaca, N. Y., USA

SO Inorg. Chem. (1974), 13(8), 1956-60
CODEN: INOCAJ

DT Journal

LA English

CC 67-3 (Catalysis and Reaction Kinetics)
Section cross-reference(s): 6

AB The redn. of tetrakis(4-N-methylpyridyl)porphinecobalt(III) (I) by **Cr**(II) was studied as a function of pH and added anions. In HClO4 medium, the obsd. rate const. may be written as kobs = (k0 + ko'/[H+])[Cr2+]; in the presence of Cl- and SCN-, catalytic pathways are introduced. Comparison of rate consts. with those for the redn. of tris(1,10-phenanthroline)cobalt(III), hexaamminecobalt(III), and tetrakis(4-pyridyl)porphineiron(III) leads to the conclusion that the acid-dependent pathways involve hydroxy-bridged transition states and that redn. of I occurs through the axially bound ligands rather than through the porphyrin ring system. The redn. of the Co(III) porphyrin proceeds faster than the replacement of the axial H2O mols. by Cl- or SCN- ions and, therefore, in contrast to the situation for the Fe(III) porphyrin which undergoes rapid **ligand replacement**, the added anions are not directly bonded to the Co(III) center in the transition state for the redn. These studies show that the mechanism of electron transfer in these porphyrin systems is largely detd. by the ease of **ligand replacement** at the metal center.

ST cobalt porphine redn **chromium**

IT Kinetics of reduction
Reduction
(of cobalt and iron complexes with porphine derivs.)

IT 22541-79-3, reactions
RL: RCT (Reactant)
(redn. by, of iron and cobalt porphine deriv. complexes)

IT 302-04-5 16887-00-6
RL: RCT (Reactant)
(redn. of cobalt porphyrin complex by **chromium**(2+) in presence of)
IT 51329-41-0 51371-92-7
RL: RCT (Reactant)
(redn. of, by **chromium** ion, kinetics and mechanism of)

L2 ANSWER 13 OF 14 CA
AN 75:91806 CA
TI Heteronuclear transition metal complexes. II. Chelating diphosphine and diarsine palladium and platinum di-.mu.-organothiotetracarbonyls of Group VI, L-LM'(SR)2M(CO)4
AU Braterman, P. S.; Wilson, V. A.; Joshi, K. K.
CS Dep. Chem., Univ. Glasgow, Glasgow, Scot.
SO J. Organometal. Chem. (1971), 31(1), 123-9
CODEN: JORCAI
DT Journal
LA English
CC 68 (Phase Equilibriums, Chemical Equilibriums, and Solutions)
AB Members of the series L-LM'(SR)2M(CO)4 L-L = 1,2-bis(diphenylphosphino)ethane, o-phenylenebis(diethylarsine); M' = Pd, Pt; R = Me, Ph; M = **Cr**, Mo, W% were prepd. by **ligand replacement** reactions. The complexes, although highly stable as solids, decomp. rapidly in soln. From their ir and diffuse reflectance electronic spectra there is evidence that the complexes L-LM'(SR)2 behave simply as chelating disulfide ligands; in contrast to the complexes (.pi.-C5H5)2Ti(SR)2M(CO)4, there is no evidence for any metal-metal bonding.
ST diarsine metal complexes; diphosphine metal complexes; arsine metal complexes; phosphine metal complexes; transition metal complexes; **chromium** chelates; molybdenum chelates; tungsten chelates; palladium chelates; platinum chelates
IT Carbonyls
RL: PRP (Properties)
(transition metal)
IT Arsine, o-phenylenebis[diethyl-, platinum metal complexes
Phosphine, ethylenebis[diethyl-, platinum metal complexes
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
IT 33971-04-9P 33971-05-0P 33971-06-1P 33971-07-2P 33971-08-3P
33971-09-4P 33971-10-7P 33971-11-8P 33971-12-9P 33971-13-0P
33971-14-1P 33971-43-6P 33971-44-7P 33971-45-8P 33971-46-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

L2 ANSWER 14 OF 14 CA
AN 73:72662 CA
TI Reaction mechanisms in molten salts. I. **Ligand replacement** in **chromium**(III) complexes dissolved in hydrogen sulfate melt and in 100% sulfuric acid
AU Duffy, John A.; Macdonald, W. J. D.
CS Dep. Chem., Univ. Aberdeen, Old Aberdeen, Scot.
SO J. Chem. Soc. A (1970), (12), 2066-71
CODEN: JCSIAP
DT Journal
LA English
CC 78 (Inorganic Chemicals and Reactions)
AB Spectral shifts in the crystal-field bands of a variety of **Cr**(III) complexes dissolved in 100% H2SO4 at 40.degree. show that the ligands H2O, oxalate, acetylacetonate, and chloride, but not NH3 and ethylenediamine, are easily substituted by (protonated) sulfate ligands. By selecting appropriate ligands in the coordination sphere, it is possible to generate and record the spectra of the (solvated) species

Cr(en)33+, **Cr**(en)23+, **Cr**(en)3+, and Cr3+ in
100% H2SO4. These data are used for studying the decompn. of the [
Cr(en)3]3+ ion in molten NH4HSO4-KHSO4 at 142.degree.. The 1st
and 2nd ethylenediamine ligands are removed rapidly from the coordination
sphere, and removal of the 3rd is probably a 1-stage process. Comparison
is made with the decompn. of the complex in 100% H2SO4 at the same temp.

ST reaction mechanisms molten salts; molten salts reaction mechanisms;
chromium complexes ligand rplacement; **ligand**
replacement chromium complexes; sulfate ligands
chromium complexes

IT Ammines
RL: RCT (Reactant)
(**chromium**, substitution reaction of, with hydrogen sulfate
ion)

IT Salts, reactions
RL: RCT (Reactant)
(**ligand replacement** mechanisms in molten)

IT Substitution reactions
(of ligands, in **chromium** complexes)

IT 2,4-Pentanedione, **chromium** complexes
Ethylenediamine, **chromium** complexes
RL: RCT (Reactant)
(substitution reaction of, with hydrogen sulfate ion)

IT 10141-00-1
RL: RCT (Reactant)
(reaction of, with sulfuric acid)

IT 338-70-5, reactions
RL: RCT (Reactant)
(substitution reaction of, with hydrogen sulfate in **chromium**
complexes)

IT 13681-82-8 13820-89-8 14023-00-8 14217-01-7 14301-97-4
14493-60-8 15363-28-7 15654-71-4 19683-62-6 28939-22-2
29046-77-3
RL: RCT (Reactant)
(substitution reaction of, with sulfate)